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Polymer 46 (2005) 6148–6153
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Characterization of capacitance–frequency features of Sn/polypyrrole/n-Si structure as a function of temperature

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Received 12 February 2005; received in revised form 26 April 2005; accepted 30 April 2005
Available online 16 June 2005

Abstract

Temperature-dependent, the capacitance–frequency measurements of Sn/polypyrrole/n-Si structure have been carried out by using the Schottky capacitance spectroscopy (SCS) technique. It has seen that capacitance almost independent of temperature up to a certain value of frequency but the capacitance decrease at high frequencies. Besides, the interface states densities show a decrease with bias from the bottom of the conduction band towards the midgap at different temperature. The values of relaxation time have been higher towards the low temperature. The higher values of capacitance at low frequencies were attributed to the excess capacitance resulting from the interface states in equilibrium with the n-Si that can follow the Ac signal.
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Keywords: Polypyrrole; Interface state of density; Relaxation time

1. Introduction

Electronically conducting or semiconducting polymers have currently received significant attention [1–4] as new functionality organic materials applicable to Schottky diodes [5], field effect transistors (FETs) [6–9] or organic transistors [10], batteries [11], light emitting diodes [12] and polymeric thin capacitors [13–15]. For example, many devices using the polymeric materials [16–22] have been fabricated including light-emitting diodes and Schottky type interfaces between an inorganic semiconductor/organic semiconductor compound or a metal/organic semiconductor compound, and their electrical and photoelectrical properties have been investigated for more than three decades [23]. The effect of the time dependent on the characteristic parameters of PPy/p-type Si/Al structure [24] and the effect of the temperature on the characteristic parameters of PPy/n-Si/Au–Sb structure [25] have been studied as detailed. Besides, the great advantage that polymers offer is that they are easy to fabricate directly from solution and in contrast to inorganic semiconductors do not need surfaces with regularity at the atomic level; they do not have dangling bonds [26].

Capacitance measurement is one of the most important nondestructive methods for obtaining information on rectifying contacts interfaces. In some contacts the capacitance under forward bias is larger than the space-charge capacitance predicted by basic theory. The difference between the measured and the space-charge capacitance is called the excess capacitance and is attributed to interface states. The interface states can be created by crystal lattice discontinuities (dangling bonds), interdiffusion of atoms or a large density of crystal lattice defects close to the metal/semiconductor interface [27] or conductive polymer/semiconductor interface. The interface states capacitance is a function of the forward bias current and frequency [28]. The magnitude of the capacitance related to the interface states (C_{it}) is relatively small. For low forward currents, the capacitance can be measured using standard impedance and capacitancemeters. For large forward currents, the signal related to the interface states capacitance is overwhelmed by the thermionic emission conductance and more sophisticated, high accuracy measurement techniques are required. Schottky capacitance spectroscopy (SCS) is a measurement technique which can provide the required accuracy in the interface states

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doi:10.1016/j.polymer.2005.04.102

capacitance measurements [29,30]. The technique is based one strong dependence of the semiconductor junction differential admittance on the temperature and measurement Ac signal frequency in the case of a semiconductor with an incompletely ionized impurity. In general, the *C–f* plots in the idealized case are frequency independent [31–34]. However, this idealized case is often disturbed due to the presence of the interface states at the interfacial layer and semiconductor interface [35–38]. If charge is exchanged between the interface states and the semiconductor when a small Ac signal is applied, the measured junction capacitance is the sum of the space-charge and interface states capacitance [39].

The forward bias *C–f* measurements give the important information about the density or energy distribution of the interface states of the structure. Our purpose in the present study is to compute the interface state density of polypyrrole/n-Si structure from the *C–f* characteristics as a function of temperature, at various biases. We report here how interface state density of polypyrrole/n-Si structure has changed with temperature and bias. In the present work, we used polypyrrole for the preparation of the polypyrrole/n-Si structure. The capacitance–frequency measurement of the structure have been carried out in dark, at different temperatures and at various biases.

2. Experimental procedure

In this study, n-Si wafer with (100) orientation, 400 μm thickness and 1–10 Ω cm resistivity was used and then, the n-Si wafer was chemically cleaned using the RCA cleaning procedure (i.e. 10 min boil in $NH_3+H_2O_2+6H_2O$ followed by a 10 min $HCl+H_2O_2+6H_2O$ at 60 °C) before making contacts. The ohmic contact was made by evaporating Au–Sb alloy on the back of the substrate, then was annealed at 420 °C for 3 min in N_2 atmosphere. The native oxide on the front surface of the n-Si substrate was removed in $HF+10H_2O$ solution. Finally, it was rinsed in de-ionised water for 30 s and was dried. After ohmic contact made, the ohmic contact side and the edges of the n-Si semiconductor substrate used as an anode were covered by wax so that the polished and cleaned front side of the sample (with a circle area, it has 1.7 mm diameter) was exposed to the electrolyte by mounting it in an experimental set-up employed for polymerization. A platinum plate was used as a cathode. The electrolyte was composed of 0.40 M pyrrole and 0.10 M tetrabutylammonium tetrafluoroborate. The pyrrole obtained from Fluka Chimika was used to prepare polypyrrole at room temperature. The electrolyte solution was prepared in a propylene carbonate solvent (Merck trademark). The polymer film was electrochemically deposited on surface of the sample under an electrolyte constant temperature of 45 °C and a constant current conditions of 4 mA. After polymerization process was carried out, the surface coated polypyrrole was cleaned by acetonitrile for 10 min at room temperature and was dried. Then to perform the electrical measurements Sn was evaporated on the polypyrrole at 10^{-5} Torr. In this way the Sn/PPy/n-Si structure was obtained. A schematic cross-section of the sample holder together with the Sn/PPy/n-Si structure is shown in Fig. 1. The *C–f* measurements of this structure were measured with an HP4192A LF capacitance-meter, at the various bias(0.00–0.26 V) with steps of 0.02 V and various temperature by using a homemade liquid nitrogen cryostat equipped with a temperature controller in darkness.

3. Results and discussion

As explained above, Schottky capacitance spectroscopy is a widely used method which determines the variation of the interface state capacitance as a function of the forward bias at low frequency [40–42]. The capacitance of the devices depending on frequency is given as follows [40,41,43];

$$C = C_{sc} + C_{ss} \quad \text{(at low frequency)} \tag{1}$$

$$C \cong C_{sc} \quad \text{(at high frequency)} \tag{2}$$

where C_{sc} is space charge capacitance, and C_{ss} is interface capacitance.

The interface capacitance can be described as [41]

$$C_{ss} = AqN_{ss}\frac{\text{Arctan}(wt)}{w\tau} \tag{3}$$

where τ is the time constant and can be written as

$$\tau = \frac{1}{v_{th}\sigma N_d}\exp\left(\frac{qV_d}{kT}\right) \tag{4}$$

where σ is the cross section of interface states, v_{th} is the thermal velocity of the carrier, N_d is doping concentration, q is electron charge and k is Boltzmann constant. The interface state density for small values of $\omega\tau$ is equal to [40,42,43]

$$N_{ss} = \frac{C_{ss}}{qA} \tag{5}$$

(A is the diode area). The interface state capacitance (C_{sc}) is determined from the vertical axis intercept of *C–f* plots.

In n-type semiconductors, the energy of the interface

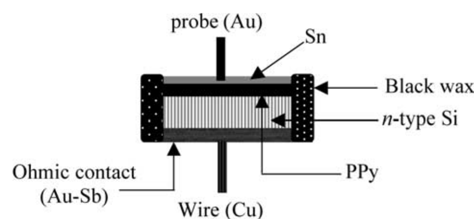

Fig. 1. A schematic cross-section of the sample holder and Sn/PPy/n-Si/Au–Sb structure.

states, E_{ss}, with respect to the bottom of conduction band at the surface of the semiconductor is given by [38]

$$E_c - E_{ss} = q(\Phi_b - V) \quad (6)$$

where E_c is the bottom of the conduction band, Φ_b is the barrier height and V is the bias voltage.

Figs. 2–4 show the measured capacitance as a function of frequency with steps of 0.02 V as a parameter at $V = 0.00$, 0.10 and 0.20 V, respectively. As can be seen these figures, the capacitance is weakly dependent on frequency especially low temperatures. When the frequency was increased further, the capacitance shows strong frequency dependence and tends to decrease more rapidly. Generally, the capacitance measured for a Schottky diode is dependent on the reverse bias voltage and frequency. The voltage and frequency dependence is due to the particular features of a Schottky barrier, impurity level, high series resistance, etc. At low frequency, the capacitance measured is dominated by the depletion capacitance of the Schottky diode, which is bias-dependent and frequency-independent. As the frequency is increased, the total diode capacitance is affected not only by the depletion capacitance, but also by the bulk resistance and the dispersion capacitance, which is frequency-dependent and associated with hole or electron emission from slowly responding deep impurity levels [27, 44]. Because of these effects, the capacitance dependence on bias becomes less pronounced [45].

Figs. 5–7 show the experimental *C–f* characteristics with bias voltage as a parameter of the Sn/PPy/n-Si structure (with steps of 0.02 V) at $T = 300$, 220 and 130 K, respectively. It can be seen these figures, especially the values of capacitance are higher at the high temperatures with respect to the low temperatures. Also, the values of the measured capacitance are become almost constant up to the certain frequency values towards to the lower temperature.

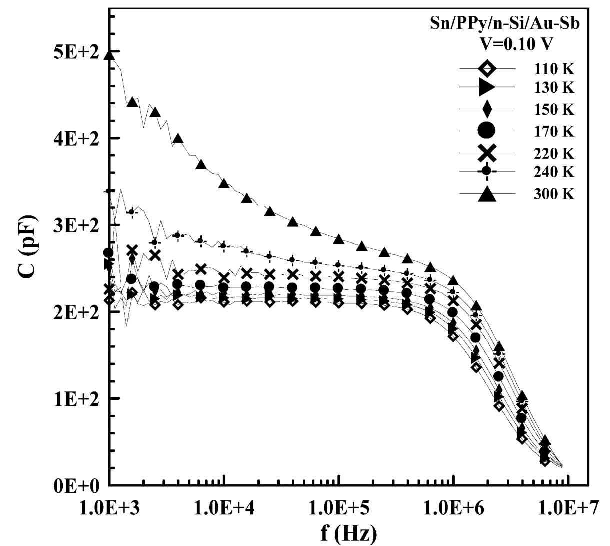

Fig. 3. $V = 0.10$ V bias the *C–f* characteristics of Sn/PPy/n-Si structure as a function of temperature.

Namely, the values of capacitance are almost independent of temperature at low temperatures (below 220 K). This behavior can be explained by the freezeout of trapping and detrapping phenomena at interface states acting as recombination centres [46]. According to these figures, the higher values of capacitance at low frequency and high temperature are due to the excess capacitance resulting from the interface states in equilibrium with the n-type Si that can follow the Ac signal.

In general, it can be seen that there are two regions for the *C–f* characteristics. Therefore, we can say that at low frequencies, the conductance is constant and it similar to the dc value. The second region (at high frequencies) is seen to vary and it has been suggested that this region is

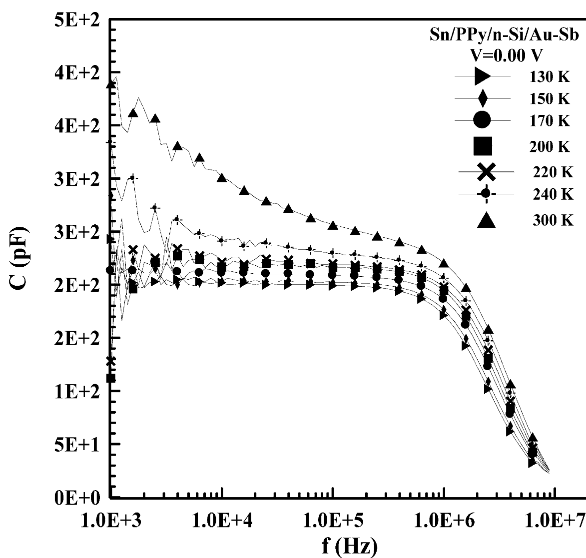

Fig. 2. Zero bias the *C–f* characteristics of Sn/PPy/n-Si structure as a function of temperature.

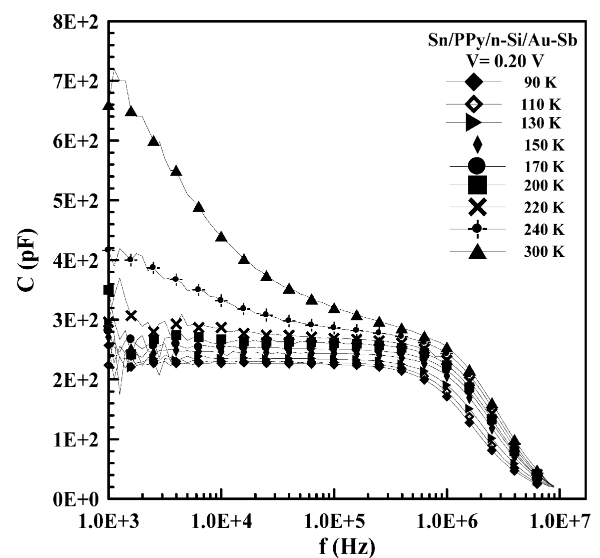

Fig. 4. $V = 0.20$ V bias the *C–f* characteristics of Sn/PPy/n-Si structure as a function of temperature.

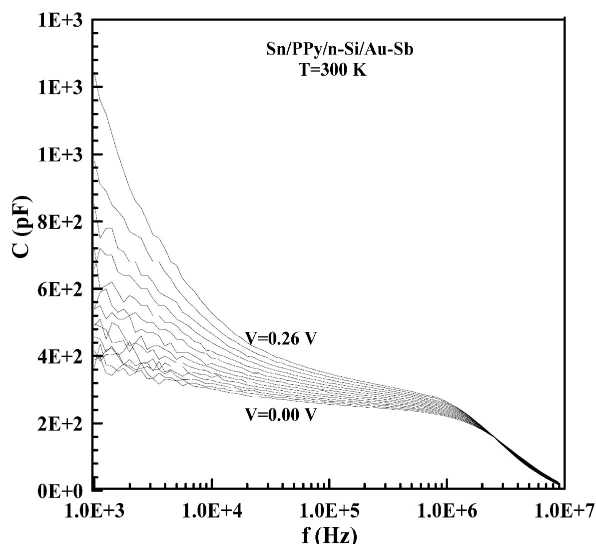

Fig. 5. The experimental C–f curves of the Sn/PPy/n-Si structure (0.00–0.26 V with steps of 0.02 V) at $T=300$ K.

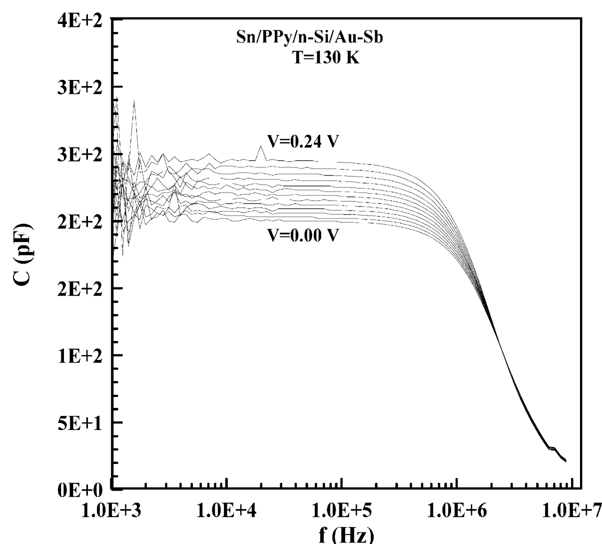

Fig. 7. The experimental C–f curves of the Sn/PPy/n-Si structure (0.00–0.24 V with steps of 0.02 V) at $T=130$ K.

characteristics of trapped carriers hopping between filled and empty states at the Fermi level [47].

Figs. 8–10 show the experimental the N_{ss} versus E_{ss} and τ versus E_c-E_{ss} plots, obtained from C–f characteristics, at $T=300$, 220 and 130 K, respectively. For this, we used the SCS method. As can be seen from Fig. 8, the interface state density N_{ss} obtained by the SCS method ranges from 8.0×10^{10} cm^{-2} eV^{-1} in 0.71 eV to 2.0×10^{13} cm^{-2} eV^{-1} in 0.45 eV. In Fig. 9, the values of N_{ss} varies from 1.0×10^{12} cm^{-2} eV^{-1} in 0.65 eV to 8.8×10^{12} cm^{-2} eV^{-1} in 0.39 eV and in Fig. 10, the values of N_{ss} varies from 1.3×10^{12} cm^{-2} eV^{-1} in 0.49 eV to 8.0×10^{13} cm^{-2} eV^{-1} in 0.39 eV. The values of the relaxation time for the device show a decrease with bias from the bottom of the conduction band towards the midgap, from 2.0×10^{-4} s in 0.71 eV to 40×10^{-4} s in 0.45 eV (for 300 K), from 69×10^{-4} s in 0.65 eV to 1.0×10^{-1} s in 0.39 eV (for 220 K) and from 28×10^{-3} s in 0.49 eV to 1.7 s in 0.25 eV (for 130 K). Besides, it can be seen that the variation of the relaxation time is slower at high temperature than low temperature.

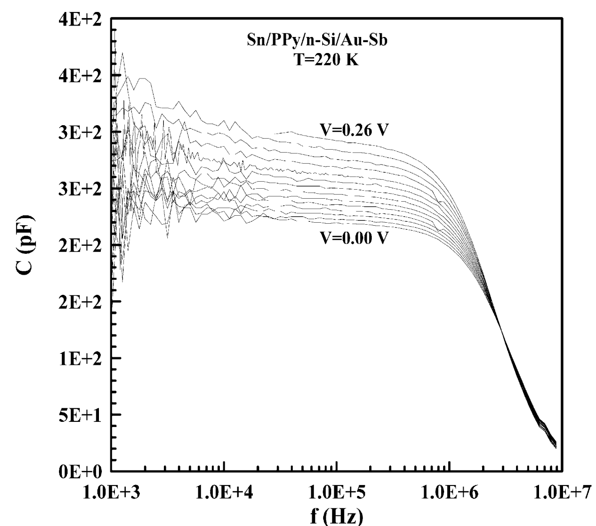

Fig. 6. The experimental C–f curves of the Sn/PPy/n-Si structure (0.00–0.26 V with steps of 0.02 V) at $T=220$ K.

In polymer/semiconductor contact applications, in order to keep the technological difficulties and unknowns to a minimum, silicon is generally chosen as the substrate semiconducting material. In this structure deposition of polymers on the inorganic semiconductor can generate large number of interface states at the semiconductor surface that strongly influence the properties of the PPy/n-Si structure. When this structures are considered as Schottky diodes, the diodes comprises a high-resistivity layer (the depletion layer) in series with a low-resistivity layer, which has its own capacitance and resistance. In addition, the native oxide layer, which is occurred the cleaning procedure, between polypyrrole and n-Si can effect the capacitance.

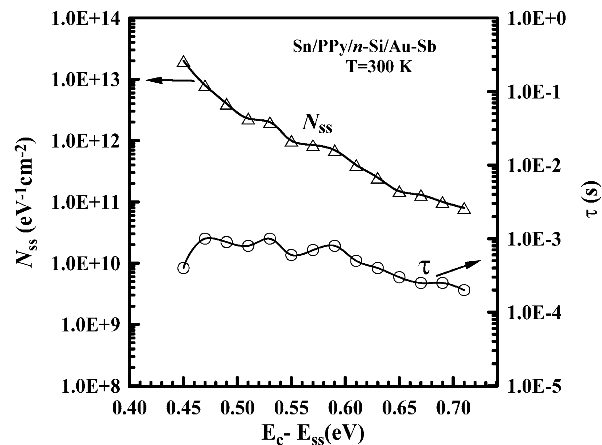

Fig. 8. The distribution plots of the interface density states and their time constant obtained from the C–f characteristics at $T=300$ K.

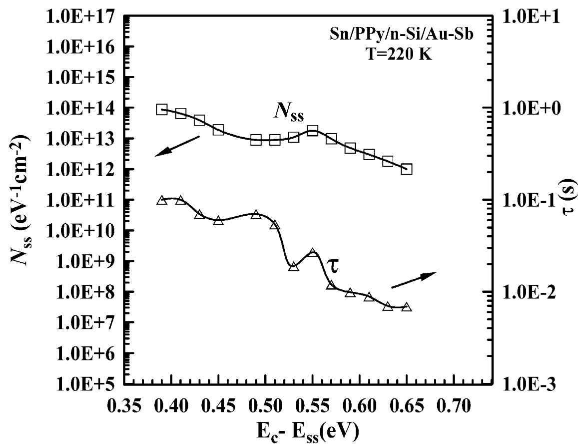

Fig. 9. The distribution plots of the interface density states and their time constant obtained from the *C–f* characteristics at $T=220$ K.

The source of charge of density N_{ss} due to dangling bond at the n-Si surface is the interfacial region of thickness that is due to the native oxide that typically exists at the inorganic semiconductor surface. The tunnel-transparent oxide layer allows charge transfer between the PPy and the n-Si. The chemical interaction at the interface of the PPy to the n-Si as at the other oxide–organic interface states will give rise to new interface states. In addition, the temperature variation modifies the equilibrium statistics in the semiconductor, changes the interface layer carrier mobility which is temperature dependent and perturbs the interface trap occupancy.

It can be said that the conductive polymer(PPy) /semiconductor(n-Si) structure can be evaluated the same as metal/semiconductor contacts. Moreover, conductive polymers can be obtained more easily than metals and semiconductors, especially with this technique. Electropolymerization of conducting polymers from suitable electrolyte is a standard method for the production of materials such as polypyrrole. The method is highly controllable, and produces thin films suitable for electrical, structural and optical characterization. Additionally, given the correct electrodes, it should, in principle, be possible to deposit conducting or photoactive polymer layers directly into a device. Also, it was seen that this technique enables us to calculate various rectifying contact parameters with a trust accurate and it is much cheaper, easy and quick to do, is very selective. While conductive polymers will probably not rival the efficiency of currently used materials, like silicon, for example in FETs, they will open up opportunities for applications where cheap and robust electronic and optoelectronic devices are required. Research on conductive polymers is closely related to the rapid development in molecular electronics. In the future it will be able to produce integrated circuits and other electronic devices.

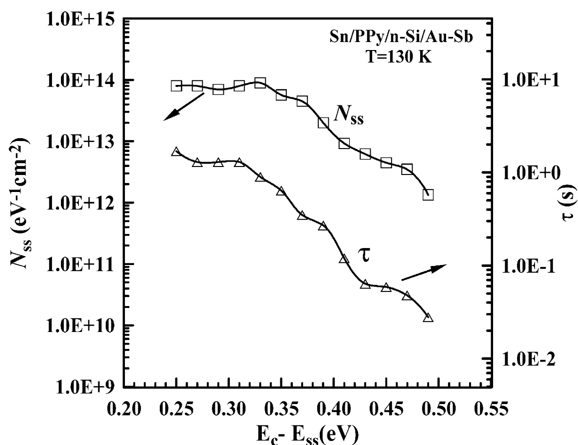

Fig. 10. The distribution plots of the interface density states and their time constant obtained from the *C–f* characteristics at $T=130$ K.

In conclusion, the study of capacitance variations with frequency, bias voltage and temperature of PPy/n-Si structure was investigated. It was seen that the values of capacitance almost independent of temperature up to a certain value of frequency, after this value, the capacitance decrease. The higher value of capacitance at low frequencies were attributed to the excess capacitance resulting from the interface states in equilibrium with the n-Si that can follow the Ac signal. The interface states density and the relaxation times were evaluated from the *C–f* plots. It was seen that interface states densities show a decrease with bias from the bottom of the conduction band towards the midgap at various temperature. Besides, the values of relaxation time have been higher towards the low temperature due to reducing the carrier mobility.

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